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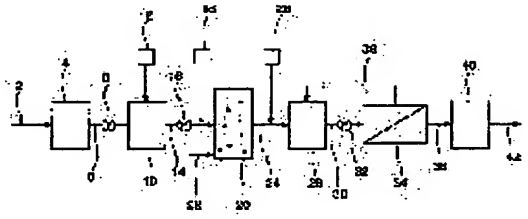
(54) WATER TREATMENT METHOD

(57)Abstract:

PURPOSE: To improve the membrane filtering efficiency of a separation membrane while performing membrane separation treatment without stopping the operation of a membrane separator when the biologically treated water from an aerobic biological membrane treatment apparatus is treated with the membrane separator while achieving the keeping of the high flux of the membrane separator, the reduction of chemical washing frequency, the enhancement of water treatment efficiency and the stable operation of a water treatment system.



CONSTITUTION: Aq. hydrogen peroxide is added to the water biologically treated in an aerobic biological membrane treatment apparatus 20 from an aq. hydrogen peroxide injection unit 26 and the concn. of hydrogen peroxide in the biologically treated water is set to 1-100mg/l. Subsequently, the biologically treated water is introduced into a membrane separator 34. Or, at the time of the backwashing of the membrane separator 34, aq. hydrogen peroxide is added to backwashing water so that the concn. of hydrogen peroxide is set to 1-100mg/l.

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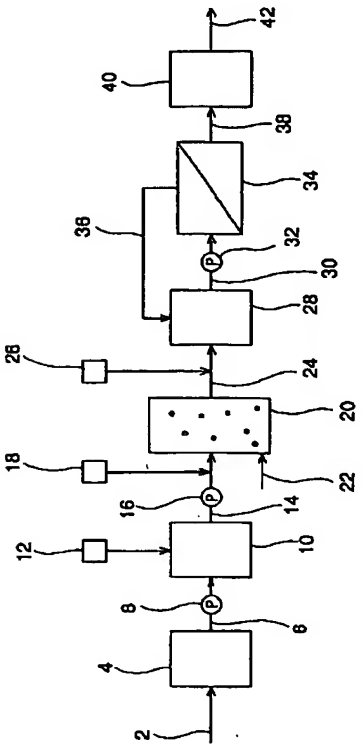

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the water treatment approach which can be used especially effective in recovery of the ultrapure water for washing in a chip fabrication factory etc., and reuse about the water treatment approach of processing further the biological treatment water which performed processing by the aerobic organism film processor with the membrane separation device using a demarcation membrane.
[0002]
[Description of the Prior Art] At a chip fabrication factory or liquid crystal works, although ultrapure water is used as variable water for washing etc., collecting and reusing wastewater of this ultrapure water from reservation of water resources and a viewpoint of a cost cut in recent years is performed. Under the present circumstances, in the recycled water of ultrapure water, since the one to 10 mgC/l. [about] organic substance contains as TOC, after removing the organic substance from recycled water, processing by the demarcation membrane, activated carbon, ion exchange resin, etc. is performed, and it is reusing as pure water or ultrapure water. Although the high-pressure UV oxidation system was used abundantly as a removal means of the organic substance contained in recycled water if cut, recently, use of the lower aerobic organism film processor of a running cost is proposed.
[0003] When building an aerobic organism film processor into an ultrapure water recovery system, membrane separation devices, such as membrane filter equipment and ultrafiltration membrane equipment, are installed in the latter part of an aerobic organism film processor for the purpose of cell separation, but when a membrane separation device is installed in the latter part of an aerobic organism film processor in this way, the demarcation membrane of a membrane separation device is polluted and membrane filtration effectiveness tends to fall. That is, by biological slime processing of low organic substance concentration like the aerobic organism membrane process in an ultrapure water recovery system, in order for subnutrition nature bacteria to have priority and to secrete many fungus body metabolite, such as proteins and polysaccharide, as the property, it is thought that the blinding of a demarcation membrane arises with a fungus body and fungus body metabolite.
[0004] Therefore, in the ultrapure water recovery system which installed the membrane separation device in the latter part of an aerobic organism film processor, although TOC of the biological treatment water from an aerobic organism film processor is falling to 0.3 to 1 mgC/about l., the rapid differential pressure between film may produce it in a demarcation membrane by contamination by the fungus body and fungus body metabolite.
[0005] Therefore, while washing conventionally the demarcation membrane using film permeated water, the compressed air, etc. as an operating method of the membrane separation device of the ultrapure water recovery system mentioned above intermittently with a fixed time interval (back wash), when the above differential pressure between film arises to some extent in a demarcation membrane, demarcation membrane washing using a chemical was carried out and the differential pressure between film is recovered. That is, in the conventional ultrapure water recovery system, by the back wash performed with a fixed time interval, and chemical washing performed when a demarcation membrane is polluted with this back wash by unremovable extent, the membrane filtration effectiveness of a demarcation membrane is improved and the processing effectiveness of

recycled water is raised.
[0006]
[Problem(s) to be Solved by the Invention] However, the chemical washing process mentioned above needs to stop the water flow to a membrane separation device, and needs to perform it, and, moreover, the long duration of about 3 - 6 hours is required. Therefore, performing chemical washing makes the processing effectiveness of recycled water fall. Therefore, a means by which the membrane filtration effectiveness of a demarcation membrane can be improved is desired, without performing chemical washing.
[0007] The approach of adding chlorinated pesticides, such as a sodium hypochlorite, in biological treatment water, and supplying to a membrane separation device as an approach of on the other hand improving the membrane filtration effectiveness at the time of performing membrane separation of biological treatment water, is proposed. However, by this approach, a chlorinated pesticide and the organic substance may react underwater and organochlorine compounds, such as a trichloroethylene, may be generated. Thus, with the ion exchange unit and reverse osmotic membrane equipment which were installed in the latter part of a membrane separation device in the ultrapure water recovery system, when an organochlorine compound generates, since the elimination factor of an organochlorine compound is bad, the water quality of the pure water obtained or ultrapure water deteriorates. Moreover, adding chlorine will give an ion load to latter ion exchange resin, and this approach is not desirable, when only to a demarcation membrane with high endurance to chlorine, and using it by the ultrapure water recovery system.
[0008] This invention was developed as a means to solve these actual condition, it can improve the membrane filtration effectiveness of a demarcation membrane, performing membrane-separation processing without suspending operation of a membrane separation device, when carrying out membrane-separation processing of the biological treatment water by the aerobic organism film processor with a membrane separation device, and aims at offering the water treatment approach of not making an organochlorine compound generating like the approach of moreover adding a chlorinated pesticide in biological treatment water.
[0009]
[Means for Solving the Problem] After this invention person added hydrogen peroxide solution in the water introduced into a membrane separation device as a result of inquiring wholeheartedly, in order to attain the above-mentioned purpose, and he made this underwater hydrogen-peroxide concentration the specific range, when a membrane separation device is supplied, he finds out that the membrane filtration effectiveness of a demarcation membrane is improved effectively, and came to make this invention.
[0010] That is, this invention offers the water treatment approach characterized by supplying this biological treatment water to a membrane separation device, after adding hydrogen peroxide solution in the water treatment approach of processing the biological treatment water which performed processing by the aerobic organism film processor as the 1st invention with a membrane separation device so that hydrogen-peroxide concentration may become said biological treatment water in l. and 1-100mg /(claim 1).
[0011] Moreover, this invention offers the water treatment approach characterized by performing the back wash of a demarcation membrane with this wash water for back washes, after adding hydrogen peroxide solution in performing the back wash of the demarcation membrane of said membrane separation device in the water treatment approach of processing the biological treatment water which performed processing by the aerobic organism film processor as the 2nd invention with a membrane separation device so that hydrogen-peroxide concentration may become wash water for back washes in l. and 1-100mg /(claim 2).
[0012] Hereafter, it explains to a pan in detail per this invention. In this invention, the biological treatment water which performed processing by the aerobic organism film processor is processed with a membrane separation device. In this case, as an aerobic organism film processor, the biological slime processor using the thing in which the aerobic organism film was formed on microorganism adhesion support, such as granular active carbon, spherical activated carbon, and fibrous activated carbon, is mentioned, for example. Moreover, as a membrane separation device, what used a membrane filter (MF), ultrafiltration membrane (UF), a reverse osmotic membrane

(RO), etc. as a demarcation membrane is mentioned, for example. As a configuration of a demarcation membrane, the shape of the shape of a hollow filament and a spiral and tubular ** are mentioned.

[0013] In this invention, hydrogen peroxide solution is added in these water so that the hydrogen-peroxide concentration biological treatment underwater (the 1st invention) or in the wash water for back washes (the 2nd invention) may become in l. and 1-100mg /. The l. of the improvement effect of membrane filtration effectiveness is [hydrogen-peroxide concentration] inadequate in less than 1mg /. Moreover, if hydrogen-peroxide concentration exceeds l. in 100mg /, while destruction of a fungus body will become remarkable and membrane filtration effectiveness will worsen on the contrary, the water quality of film permeated water deteriorates. 5-80mg /especially of more desirable values of the hydrogen-peroxide concentration of biological treatment water or the wash water for back washes is [l.] 40-60mg/l.

[0014] In the 1st invention, addition of the hydrogen peroxide solution to biological treatment water may be performed continuously, and you may carry out intermittently. These are suitably determined in consideration of the degree of an improvement of the membrane filtration effectiveness by addition of the hydrogen peroxide solution to biological treatment water. Moreover, in consideration of the degree of an improvement of membrane filtration effectiveness, it decides on the addition time interval in the case of adding hydrogen peroxide solution intermittently, and addition time amount similarly.

[0015] The mode which adds hydrogen peroxide solution continuously is also employable as biological treatment water until it starts addition of the hydrogen peroxide solution to biological treatment water and the differential pressure between film falls to a desirable value succeedingly as a mode which adds hydrogen peroxide solution in biological treatment water, after the differential pressure between film of a demarcation membrane goes up from a predetermined value. According to this mode, it is possible to recover the differential pressure between film, performing the water flow to a membrane separation device, and to improve membrane filtration effectiveness.

[0016] In the 2nd invention, film permeated water and processed water of a membrane separation device, or other wash water is mentioned as wash water for back washes which adds hydrogen peroxide solution. A periodical back wash is performed about 2 to 3 minutes, after carrying out predetermined time at intervals of predetermined time and performing membrane separation for about 30 to 60 minutes. It is desirable to add hydrogen peroxide solution to the wash water for back washes in the 2nd invention at the time of all back washes. That is, since a back wash is performed by high frequency, an improvement of membrane filtration effectiveness can be effectively attained by adding hydrogen peroxide solution to the wash water for back washes for whenever [of a back wash / every]. However, addition of the hydrogen peroxide solution to the wash water for back washes may be performed only at the time of some back washes, and these are chosen in consideration of the degree of an improvement of the membrane filtration effectiveness by addition of the hydrogen peroxide solution to the wash water for back washes.

[0017] In this invention, it may be made to perform both addition of the hydrogen peroxide solution to the biological treatment water at the time of membrane-separation processing, and addition of the hydrogen peroxide solution to the wash water for back washes at the time of a back wash.

[0018] The water treatment approach of this invention is an especially effective approach, when processing and reusing the recycled water of ultrapure water. Moreover, it is applicable also to processing of water with comparatively low TOC concentration like the complete treatment of wastewater, or processing of purification plant.

[0019]

[Function] In the recycled water of the ultrapure water used at a chip fabrication factory or liquid crystal works, the one to 10 mgC/l. [about] organic substance contains as TOC. Although the aerobic organism membrane process using subnutrition nature bacteria is an effective means as a means to disassemble these organic substance, in the biological treatment underwater, a lifting, a cone fungus body, and fungus body metabolite contain the blinding of a latter demarcation membrane so much. Although the approach of adding a chlorinated pesticide is in biological treatment water as an approach of mentioning membrane filtration effectiveness when performing membrane separation of such biological treatment water, by this approach, an organochlorine

compound may be generated and an ion load is given to latter ion exchange resin.
[0020] On the other hand, after pouring hydrogen peroxide solution into the biological treatment water which performed processing by the aerobic organism film processor and carrying out [l.] hydrogen-peroxide concentration in 1-100mg /, by letting water flow to a film filter, the adhesion force to the multiplication and the film of a microorganism can be weakened, and a hydrogen peroxide can perform oxidative degradation of the gel on a film surface, and the blinding matter in the film. And membrane filtration effectiveness improves according to such effectiveness, and it becomes reduction of the chemical washing frequency of a demarcation membrane, and maintainable [high flux]. And the organochlorine compound to which the water quality of treated water is reduced does not generate.
[0021] Moreover, after adding hydrogen peroxide solution so that hydrogen-peroxide concentration may become the wash water for back washes used at the time of the usual back wash of a membrane separation device, for example, film permeated water, and processed water in l. and 1-100mg /, also in the approach of performing the back wash of a demarcation membrane, the same effectiveness can be acquired with this wash water for back washes.
[0022] In addition, using a hydrogen peroxide by 1% or more of concentration as a component of chemical washing performed when a demarcation membrane carries out blinding conventionally is known. Moreover, although the germicidal action of a hydrogen peroxide is also known, in order to expect effectiveness, 10% or more of high concentration is needed. However, the effectiveness which impregnation of the hydrogen peroxide solution of an about 1-100mg [/l.] minute amount to biological treatment water or the wash water for back washes exerts on membrane filtration effectiveness was not examined until now.
[0023] Then, this invention person considered impregnation of the hydrogen peroxide solution of the minute amount to biological treatment water or the wash water for back washes, and relation between the hydrogen-peroxide concentration at that time, and a membrane filtration property improvement effect. Consequently, the optimal hydrogen-peroxide concentration for raising membrane filtration effectiveness exists, therefore it finds out that a membrane filtration property is improvable, performing the usual membrane-separation processing which consists of water flow to the membrane separation device of biological treatment water, and a back wash of a demarcation membrane by introducing into a membrane separation device, after making hydrogen-peroxide concentration of biological treatment water or the wash water for back washes into the optimal above-mentioned range, and this invention is completed.
[0024]
[Example] Hereafter, although an example shows this invention concretely, this invention is not limited to the following example. Drawing 1 R> 1 is the flow Fig. showing an example of the water treatment system used for operation of this invention approach. This water treatment system is an ultrapure water recovery system which performs water treatment by using as raw water the recycled water of the ultrapure water used for washing of a semi-conductor wafer etc. in a semi-conductor manufacture process.
[0025] In drawing 1 in 2, raw water installation tubing and 4 connection piping and 8 for a raw water tub and 6 A pump, The acid and alkali impregnation unit by which 10 was connected to pH control equipment and 12 was connected to pH control equipment 10, The nitrogen and the Lynn impregnation unit by which connection piping and 16 were connected to the pump and 18 was connected to the connection piping 14 for 14, Air installation tubing by which 20 was connected to the aerobic organism film processor, and 22 was connected to the aerobic organism film processor 20, The hydrogen-peroxide-solution impregnation unit by which 24 was connected to connection piping and 26 was connected to the connection piping 24, In 28, connection piping and 40 show a treated water tub, and, as for a biological treatment tank, circulation piping a pump and 34 circulate through the retentate of a membrane separation device 34 to membrane separation devices, such as membrane filter equipment, ultrafiltration membrane equipment, and reverse osmotic membrane equipment, and 30 circulates through 36 in the biological treatment tank 28 as for whose connection piping and 32, and 38, 42 shows a treated water exhaust pipe. In addition, the circulation piping 36 is formed as occasion demands according to the class of membrane separation device 34.
[0026] Water treatment by this system is performed as follows.

(1) Water is supplied to the raw water introduced into the raw water tub 4 from the raw water installation tubing 2 by the pH neutralization tank 10, and from an acid and the alkali impregnation unit 12, an acid or alkali is added and it is neutralized here. The water after neutralization is supplied to the aerobic organism film processor 20, after initial-complement addition of nitrogen and Lynn required for biological treatment is carried out by nitrogen and the Lynn impregnation unit 18.
[0027] (2) In the aerobic organism film processor 20, in order to supply oxygen required for biological treatment, biological treatment is performed by work of the microorganism which grew on the front face of the microorganism adhesion support with which the interior is filled up where air is blown into processed underwater one from the air installation tubing 22. Thereby, the processed underwater organic substance is disassembled.
[0028] (3) Hydrogen peroxide solution is added from the hydrogen-peroxide-solution impregnation unit 26 by the biological treatment water into which the organic substance was disassembled. Thereby, biological treatment underwater hydrogen-peroxide concentration is adjusted [l.] in 1-100mg /. In this case, addition of the hydrogen peroxide solution to biological treatment water may be performed continuously, and you may carry out intermittently.
[0029] (4) The biological treatment water with which hydrogen peroxide solution was added is supplied to a membrane separation device 34 through the biological treatment tank 28, and membrane separation is performed. In this case, in this system, since the hydrogen peroxide with a concentration of 1-100mg [/l.] contains in biological treatment water, the membrane filtration effectiveness of a membrane separation device 34 is improved, and membrane-separation processing is performed efficiently. the film permeated water of a membrane separation device 34 should pass the treated water tub 40 -- although discharged -- this treated water -- the need -- responding -- an activated carbon filter, reverse osmotic membrane equipment, and ion exchange resin -- processing by a column etc. is performed and it is reused as pure water and ultrapure water.
[0030] (5) Moreover, in this system, without adding the hydrogen peroxide solution to addition of the hydrogen peroxide solution to the biological treatment water mentioned above, or biological treatment water, hydrogen peroxide solution can be added so that hydrogen-peroxide concentration may become wash water for back washes in l. and 1-100mg /at the time of a back wash. In addition, this back wash is performed by making the back wash water with which hydrogen-peroxide concentration was adjusted to the above-mentioned range flow backwards from the permeated water side of a membrane separation device to a raw water supply side.
[0031] Next, the example of an experiment is shown.
In order to investigate the effectiveness which addition of the hydrogen peroxide solution to [example 1 of experiment] biological treatment water gives to the membrane filtration effectiveness of membrane filter equipment, it experimented on condition that the following.
raw water: -- water biological slime processor: which contains isopropyl alcohol 4mgC/a liter as TOC -- fixed-bed type aerobic organism film processor membrane separation device: -- the membrane separation device [0032] using the membrane filter made from polypropylene of 0.2 micrometers of apertures After carrying out biological treatment of the above-mentioned raw water with the biological slime processor and adding hydrogen peroxide solution in biological treatment water, except not adding hydrogen peroxide solution with the system [A] which performed processing by the membrane separation device, about the system [B] which performed same processing, the amount operation of steady flow (100l./m2/hr) was performed, respectively, and the differential pressure between film of a membrane separation device was measured.
[0033] However, in the system [A], hydrogen peroxide solution was continuously added in biological treatment water, addition of hydrogen peroxide solution was stopped in the 51 - 70th day so that hydrogen-peroxide concentration might become in l. and 10mg /till the 50th, and hydrogen peroxide solution was continuously added in biological treatment water in the 71 - 100th day so that hydrogen-peroxide concentration might become in l. and 10mg /again. Moreover, in the system [B], after the differential pressure between film reached 100KPa(s), hydrogen peroxide solution was continuously added in biological treatment water so that hydrogen-peroxide concentration might become [l.] in 10mg /. A result is shown in drawing 2 . In drawing 2 , B of A is as a result of a system [B] as a result of a system [A].
[0034] From the result of a system [A] and [B], by adding hydrogen peroxide solution in biological

treatment water so that hydrogen-peroxide concentration may become [l.] in 10mg /shows that the membrane filtration effectiveness of a demarcation membrane is sharply improved compared with the case where hydrogen peroxide solution is not added.
[0035] Moreover, from the result of a system [A], even if it suspended supply of hydrogen peroxide solution on the way, the differential pressure between film did not immediately go up, but even if it performed intermittently addition of the hydrogen peroxide solution to biological treatment water, it became clear that it is effective.
[0036] Furthermore, it became clear from the result of a system [B] that it is possible to wash the film and to recover the differential pressure between film which deteriorated, the fall of the differential pressure between film having been accepted, therefore continuing operation of a membrane separation device by pouring hydrogen peroxide solution into biological treatment water, when the differential pressure between film went up. Although membranous chemical washing was usually carried out by the frequency of 1 time in one - three months, it becomes possible to reduce the frequency of chemical washing in the frequency of 1 time by the above-mentioned approach in six - 12 months, and it is thought until now that it contributes to the rise of water recovery and stable operation of a recovery system greatly.
[0037] The relation between [example 2 of experiment] biological treatment underwater hydrogen-peroxide concentration and the filtration specific resistance of a demarcation membrane was considered.
biological treatment water: -- supernatant water number-of-microorganism =2x106 piece/ml membrane separation device: of the activated-sludge-treatment water using the bacillus of a mixed culture system -- membrane separation device filtration approach: using the cellulose acetate system membrane filter (ADVANTEC Co., Ltd. make) of 0.2 micrometers of apertures -- constant-pressure pressure filtration [0038] It filtered on condition that the above, changing the hydrogen-peroxide-solution addition to biological treatment water, and the relation between hydrogen-peroxide concentration and filtration specific resistance was investigated. A result is shown in drawing 3 . If membrane filtration effectiveness is improved in the range whose hydrogen-peroxide concentration is 1-100mg/l. and l. is exceeded in 100mg /from drawing 3 , it is clear that membrane filtration effectiveness worsens conversely.
[0039] On condition that below [the example 3 of an experiment], addition of the hydrogen peroxide solution to biological treatment water and addition of a hypochlorite considered the effect affect an ultrapure water manufacturing system.
raw water: -- water ultrapure water manufacturing system: which contains isopropyl alcohol 4mgC/a liter as TOC -- raw water -> biological slime processor -> ultrafiltration membrane equipment **-> activated carbon filter -> reverse osmotic membrane equipment -> ion exchange unit -> ultrafiltration membrane equipment ** biological slime processor: -- the membrane separation device [0040] using the ultrafiltration membrane made from a fixed-bed type aerobic organism film processor ultrafiltration membrane equipment ****:polyacrylonitrile In the above-mentioned ultrapure water manufacturing system, ultrapure water was manufactured, respectively by the system [X] which added hydrogen peroxide solution continuously so that hydrogen-peroxide concentration might become biological treatment water in l. and 1mg /between biological slime processor and ultrafiltration membrane equipment **s, and the system [Y] continuously added so that residual chlorine concentration might become biological treatment underwater in l. and 1mg /about a sodium hypochlorite in the same part.
[0041] Consequently, TOC of end ultrapure water (treated water after processing by ultrafiltration membrane equipment **) was 3micro gC/a liter in 1micro gC/the liter and the system [Y] in the system [X]. When the organochlorine compound in these end ultrapure water was measured by GC-MS, respectively, the organochlorine compound was not detected from the ultrapure water of a system [X]. On the other hand, from the ultrapure water of a system [Y], the trichloroethylene of about 2micro gC/a liter was detected as TOC.
[0042] It became clear for an organochlorine compound to generate by addition of the hypochlorite from the above-mentioned result to biological treatment water, and for this to leak to end ultrapure water, and to reduce the water quality. On the other hand, addition of the hydrogen peroxide solution to biological treatment water was that to which the water quality of end ultrapure water is not

reduced.
[0043]
[Effect of the Invention] The membrane filtration effectiveness of a demarcation membrane is improvable, performing the usual membrane-separation processing without according to the water treatment approach of this invention, suspending operation of a membrane separation device, when processing the biological treatment water by the aerobic organism film processor with a membrane separation device. Therefore, according to this invention, maintenance of a membrane separation device of high flux and frequency reduction of chemical washing are attained, and improvement in water treatment effectiveness and stable operation of a water treatment system can be attained. Furthermore, it leads also to a cost cut and tooth-space down of a system by raising membrane filtration effectiveness and obtaining high flux.
[0044] Moreover, this invention approach is applicable also to the demarcation membrane which does not have endurance to chlorine, when not producing the water quality fall of the pure water obtained when an organochlorine compound is not made to generate like the approach of using a chlorinated pesticide and it applies to an ultrapure water recovery system, or ultrapure water. Therefore, this invention is the very effective water treatment approach in the recovery system of the ultrapure water used as variable water of a chip fabrication factory or liquid crystal works.

[Translation done.]

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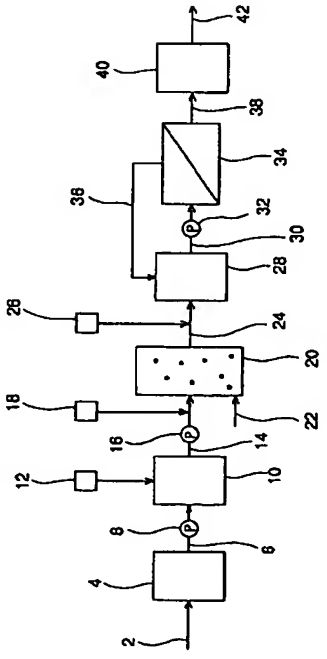
(54)【発明の名称】　水処理方法

(57)【要約】

【目的】　好気性生物膜処理装置による処理を行った生物処理水を膜分離装置で処理する場合において、膜分離装置の運転を停止することなく、膜分離処理を行いながら、分離膜の膜ろ過効率を改善する。そして、膜分離装置の高フラックスの維持、薬品洗浄の頻度低減を図り、水処理効率の向上、水処理システムの安定運転を達成する。

【構成】　好気性生物膜処理装置２０による処理を行った生物処理水に、過酸化水素水注入ユニット２６から過酸化水素水を添加し、生物処理水中の過酸化水素濃度を１～１００ｍｇ／リットルとする。次いで、この生物処理水を膜分離装置３４に導入する。あるいは、膜分離装置３４の逆洗時において、逆洗用洗浄水に過酸化水素濃度が１～１００ｍｇ／リットルとなるように過酸化水素水を添加する。



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【特許請求の範囲】

【請求項１】　好気性生物膜処理装置による処理を行った生物処理水を膜分離装置で処理する水処理方法において、前記生物処理水に過酸化水素濃度が１～１００ｍｇ／リットルとなるように過酸化水素水を添加した後、該生物処理水を膜分離装置に供給することを特徴とする水処理方法。

【請求項２】　好気性生物膜処理装置による処理を行った生物処理水を膜分離装置で処理する水処理方法において、前記膜分離装置の分離膜の逆洗を行うに当たり、逆洗用洗浄水に過酸化水素濃度が１～１００ｍｇ／リットルとなるように過酸化水素水を添加した後、該逆洗用洗浄水で分離膜の逆洗を行うことを特徴とする水処理方法。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は、好気性生物膜処理装置による処理を行った生物処理水をさらに分離膜を用いた膜分離装置で処理する水処理方法に関し、特に、半導体工場等における洗浄用超純水の回収、再利用に有効に使用することができる水処理方法に関する。

【０００２】

【従来の技術】半導体工場や液晶工場では、洗浄用等のプロセス用水として超純水が使用されているが、近年、水資源の確保及びコストダウンの観点から、この超純水の排水を回収して再利用することが行われている。この際、超純水の回収水中には、ＴＯＣとして１～１０ｍｇＣ／リットル程度の有機物が含有されているため、回収水から有機物を除去した後、分離膜、活性炭、イオン交換樹脂などによる処理を行い、純水あるいは超純水として再利用している。回収水中に含まれる有機物の除去手段としては、かっては高圧ＵＶ酸化装置が多用されていたが、最近では、ランニングコストのより低い好気性生物膜処理装置の使用が提案されている。

【０００３】超純水回収システムに好気性生物膜処理装置を組み込む場合、菌体分離を目的として、好気性生物膜処理装置の後段に精密ろ過膜装置、限外ろ過膜装置等の膜分離装置を設置するが、このように好気性生物膜処理装置の後段に膜分離装置を設置した場合、膜分離装置の分離膜が汚染され、膜ろ過効率が低下しやすい。すなわち、超純水回収システムにおける好気性生物膜処理のような低有機物濃度の生物膜処理では、低栄養性細菌が優先し、その特性として蛋白類、多糖類等の菌体代謝産物を多く分泌するため、菌体及び菌体代謝産物によって分離膜の目詰まりが生じると考えられる。

【０００４】したがって、好気性生物膜処理装置の後段に膜分離装置を設置した超純水回収システムでは、好気性生物膜処理装置からの生物処理水のＴＯＣは０．３～１ｍｇＣ／リットル程度に低下しているにもかかわらず、菌体及び菌体代謝産物による汚染によって分離膜に

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急激な膜間差圧が生じることがある。

【０００５】そのため、従来、上述した超純水回収システムの膜分離装置の運転方法としては、膜透過水や圧縮空気等を用いた分離膜の洗浄（逆洗）を一定時間間隔で間欠的に行うと共に、分離膜にある程度以上の膜間差圧が生じた時点で、薬品を用いた分離膜洗浄を実施して膜間差圧を回復している。すなわち、従来の超純水回収システムでは、一定の時間間隔で行われる逆洗と、この逆洗では除去できない程度に分離膜が汚染された場合に行われる薬品洗浄とによって、分離膜の膜ろ過効率を改善し、回収水の処理効率を向上させている。

【０００６】

【発明が解決しようとする課題】しかし、上述した薬品洗浄工程は、膜分離装置への通水を止めて行う必要があり、しかも約３～６時間という長時間を要する。したがって、薬品洗浄を行うことは、回収水の処理効率を低下させることになる。そのため、薬品洗浄を行うことなく分離膜の膜ろ過効率を改善し得る手段が望まれる。

【０００７】一方、生物処理水の膜分離を行う際の膜ろ過効率を改善する方法として、生物処理水に次亜塩素酸ナトリウム等の塩素剤を添加して膜分離装置に供給する方法が提案されている。しかし、この方法では、水中で塩素剤と有機物とが反応してトリクロロエチレン等の有機塩素化合物を生成することがある。このように有機塩素化合物が生成した場合、超純水回収システムにおいて膜分離装置の後段に設置したイオン交換装置や逆浸透膜装置では、有機塩素化合物の除去率が悪いため、得られる純水あるいは超純水の水質が低下する。また、この方法は、塩素に対して耐久性の高い分離膜にしか適用できない上、超純水回収システムにて使用する場合、塩素を添加することは後段のイオン交換樹脂に対してイオン負荷を与えることになり、好ましくない。

【０００８】本発明は、これらの実情を解決する手段として開発されたもので、好気性生物膜処理装置による生物処理水を膜分離装置で膜分離処理する場合において、膜分離装置の運転を停止することなく膜分離処理を行いながら分離膜の膜ろ過効率を改善することができ、しかも生物処理水に塩素剤を添加する方法のように有機塩素化合物を生成させることのない水処理方法を提供することを目的とする。

【０００９】

【課題を解決するための手段】本発明者は、上記目的を達成するために鋭意検討を行った結果、膜分離装置に導入する水に過酸化水素水を添加し、この水中の過酸化水素濃度を特定の範囲としてから膜分離装置に供給した場合、分離膜の膜ろ過効率が効果的に改善されることを見い出し、本発明をなすに至った。

【００１０】すなわち、本発明は、第１発明として、好気性生物膜処理装置による処理を行った生物処理水を膜分離装置で処理する水処理方法において、前記生物処理

水に過酸化水素濃度が１～１００ｍｇ／リットルとなるように過酸化水素水を添加した後、該生物処理水を膜分離装置に供給することを特徴とする水処理方法を提供する（請求項１）。

【００１１】また、本発明は、第２発明として、好気性生物膜処理装置による処理を行った生物処理水を膜分離装置で処理する水処理方法において、前記膜分離装置の分離膜の逆洗を行うに当たり、逆洗用洗浄水に過酸化水素濃度が１～１００ｍｇ／リットルとなるように過酸化水素水を添加した後、該逆洗用洗浄水で分離膜の逆洗を行うことを特徴とする水処理方法を提供する（請求項２）。

【００１２】以下、本発明につきさらに詳しく説明する。本発明では、好気性生物膜処理装置による処理を行った生物処理水を膜分離装置で処理する。この場合、好気性生物膜処理装置としては、例えば、粒状活性炭、球状活性炭、繊維状活性炭等の微生物付着担体上に好気性生物膜を形成したものを用いた生物膜処理装置が挙げられる。また、膜分離装置としては、例えば、分離膜として精密ろ過膜（ＭＦ）、限外ろ過膜（ＵＦ）、逆浸透膜（ＲＯ）等を用いたものが挙げられる。分離膜の形状としては、中空糸状、スパイラル状、管状等が挙げられる。

【００１３】本発明では、生物処理水中（第１発明）あるいは逆洗用洗浄水中（第２発明）の過酸化水素濃度が１～１００ｍｇ／リットルとなるようにこれらの水に過酸化水素水を添加する。過酸化水素濃度が１ｍｇ／リットル未満では膜ろ過効率の改善効果が不十分である。また、過酸化水素濃度が１００ｍｇ／リットルを超えると菌体の破壊が著しくなり、かえって膜ろ過効率が悪くなると共に、膜透過水の水質が低下する。生物処理水あるいは逆洗用洗浄水の過酸化水素濃度のより好ましい値は５～８０ｍｇ／リットル、特に４０～６０ｍｇ／リットルである。

【００１４】第１発明において、生物処理水への過酸化水素水の添加は、連続的に行ってもよく、間欠的に行ってもよい。これらは、生物処理水への過酸化水素水の添加による膜ろ過効率の改善の度合いを考慮して適宜決定する。また、間欠的に過酸化水素水の添加を行う場合の添加時間間隔、添加時間も、同様に膜ろ過効率の改善の度合いを考慮して決定する。

【００１５】生物処理水に過酸化水素水を添加する態様としては、分離膜の膜間差圧が所定値より上昇した後に生物処理水への過酸化水素水の添加を開始し、引き続き膜間差圧が好ましい値に低下するまで生物処理水に過酸化水素水を連続的に添加する態様を採用することもできる。この態様によれば、膜分離装置への通水を行いながら膜間差圧を回復し、膜ろ過効率を改善することが可能である。

【００１６】第２発明において、過酸化水素水を添加する逆洗用洗浄水としては、膜分離装置の膜透過水や被処理水、あるいは他の洗浄水が挙げられる。定期的な逆洗は、所定時間間隔で所定時間行うもので、例えば３０～６０分位膜分離を行ってから２～３分程度行うものである。第２発明では、全ての逆洗時において逆洗用洗浄水に過酸化水素水を添加することが好ましい。すなわち、逆洗は高い頻度で行われるので、逆洗の度毎に逆洗用洗浄水に過酸化水素水を添加することにより、膜ろ過効率の改善を効果的に達成することができる。ただし、逆洗用洗浄水への過酸化水素水の添加は一部の逆洗時にのみ行ってもよく、これらは逆洗用洗浄水への過酸化水素水の添加による膜ろ過効率の改善の度合いを考慮して選択する。

【００１７】本発明では、膜分離処理時における生物処理水への過酸化水素水の添加及び逆洗時における逆洗用洗浄水への過酸化水素水の添加の両方を行うようにしてもよい。

【００１８】本発明の水処理方法は、超純水の回収水を処理して再利用する場合に特に有効な方法である。また、排水の高度処理や浄水場の処理などのように、比較的ＴＯＣ濃度の低い水の処理にも適用可能である。

【００１９】

【作用】半導体工場や液晶工場で使用される超純水の回収水には、ＴＯＣとして１～１０ｍｇＣ／リットル程度の有機物が含有されている。これらの有機物を分解する手段としては、低栄養性細菌を利用した好気性生物膜処理が有効な手段であるが、その生物処理水中には後段の分離膜の目詰まりを起こしやすい菌体及び菌体代謝産物が多量に含有されている。このような生物処理水の膜分離を行う場合、膜ろ過効率を挙げる方法として生物処理水に塩素剤を添加する方法があるが、この方法では有機塩素化合物を生成する可能性があり、また後段のイオン交換樹脂にイオン負荷を与える。

【００２０】これに対して、好気性生物膜処理装置による処理を行った生物処理水に過酸化水素水を注入し、過酸化水素濃度を１～１００ｍｇ／リットルにした後、膜ろ過装置に通水することにより、微生物の増殖作用及び膜への付着力を弱めることができ、また過酸化水素により膜面上のゲル及び膜中の目詰まり物質の酸化分解を行うことができる。そして、これらの効果により膜ろ過効率が向上し、分離膜の薬品洗浄頻度の低減及び高フラックスの維持が可能となる。しかも、処理水の水質を低下させる有機塩素化合物が生成することもない。

【００２１】また、膜分離装置の通常の逆洗時に使用する逆洗用洗浄水、例えば膜透過水や被処理水に過酸化水素濃度が１～１００ｍｇ／リットルとなるように過酸化水素水を添加した後、この逆洗用洗浄水で分離膜の逆洗を行う方法においても、同様の効果を得ることができる。

【００２２】なお、従来、分離膜が目詰まりしたときに

行う薬品洗浄の成分として過酸化水素を１％以上の濃度で使用することは知られている。また、過酸化水素の殺菌作用も知られているが、効果を期待するためには１０％以上の高濃度を必要とする。しかし、生物処理水や逆洗用洗浄水への１～１００ｍｇ／リットル程度の微量の過酸化水素水の注入が膜ろ過効率に及ぼす効果については、これまで検討されていなかった。

【００２３】そこで、本発明者は、生物処理水や逆洗用洗浄水への微量の過酸化水素水の注入及びそのときの過酸化水素濃度と膜ろ過特性改善効果との関係について検討を行った。その結果、膜ろ過効率を向上させるのに最適な過酸化水素濃度が存在し、したがって生物処理水や逆洗用洗浄水の過酸化水素濃度を上記の最適な範囲としてから膜分離装置に導入することにより、生物処理水の膜分離装置への通水と分離膜の逆洗とからなる通常の膜分離処理を行いながら膜ろ過特性を改善できることを見い出し、本発明を完成したものである。

【００２４】

【実施例】以下、実施例により本発明を具体的に示すが、本発明は下記実施例に限定されるものではない。図１は、本発明方法の実施に用いる水処理システムの一例を示すフロー図である。この水処理システムは、半導体製造プロセスにおいて、半導体ウェハ等の洗浄に用いた超純水の回収水を原水として水処理を行う超純水回収システムである。

【００２５】図１において、２は原水導入管、４は原水槽、６は連結配管、８はポンプ、１０はｐＨ調整槽、１２はｐＨ調整槽１０に接続された酸・アルカリ注入ユニット、１４は連結配管、１６はポンプ、１８は連結配管１４に接続された窒素・リン注入ユニット、２０は好気性生物膜処理装置、２２は好気性生物膜処理装置２０に接続された空気導入管、２４は連結配管、２６は連結配管２４に接続された過酸化水素水注入ユニット、２８は生物処理水槽、３０は連結配管、３２はポンプ、３４は精密ろ過膜装置、限外ろ過膜装置、逆浸透膜装置等の膜分離装置、３６は膜分離装置３４の濃縮水を生物処理水槽２８に循環する循環配管、３８は連結配管、４０は処理水槽、４２は処理水排出管を示す。なお、循環配管３６は、膜分離装置３４の種類に応じて必要により設けられる。

【００２６】本システムによる水処理は、下記のように行われる。

（１）原水導入管２から原水槽４に導入された原水は、ｐＨ中和槽１０に送水され、ここで酸・アルカリ注入ユニット１２から酸又はアルカリが添加されて中和される。中和後の水は、窒素・リン注入ユニット１８により生物処理に必要な窒素及びリンが必要量添加された後、好気性生物膜処理装置２０に供給される。

【００２７】（２）好気性生物膜処理装置２０では、生物処理に必要な酸素を供給するために空気導入管２２から被処理水中に空気が吹き込まれた状態で、内部に充填されている微生物付着担体の表面に着生した微生物の働きによって生物処理が行われる。これにより、被処理水中の有機物が分解される。

【００２８】（３）有機物が分解された生物処理水には、過酸化水素水注入ユニット２６から過酸化水素水が添加される。これにより、生物処理水中の過酸化水素濃度が１～１００ｍｇ／リットルに調整される。この場合、生物処理水への過酸化水素水の添加は、連続的に行ってもよく、間欠的に行ってもよい。

【００２９】（４）過酸化水素水が添加された生物処理水は、生物処理水槽２８を経て膜分離装置３４に供給され、膜分離が行われる。この場合、本システムでは生物処理水に濃度１～１００ｍｇ／リットルの過酸化水素が含有されているため、膜分離装置３４の膜ろ過効率が改善され、膜分離処理が効率良く行われる。膜分離装置３４の膜透過水は、処理水槽４０を経て排出されるが、この処理水には必要に応じて活性炭塔、逆浸透膜装置、イオン交換樹脂塔等による処理が行われ、純水、超純水として再利用される。

【００３０】（５）また、本システムでは、前述した生物処理水への過酸化水素水の添加と共に、あるいは生物処理水への過酸化水素水の添加を行うことなく、逆洗時において逆洗用洗浄水に過酸化水素濃度が１～１００ｍｇ／リットルとなるように過酸化水素水を添加することができる。なお、該逆洗は、過酸化水素濃度が上記範囲に調整された逆洗水を、膜分離装置の透過水側から原水供給側に逆流させることによって行う。

【００３１】次に、実験例を示す。

［実験例１］生物処理水への過酸化水素水の添加が精密ろ過膜装置の膜ろ過効率に与える効果を調べるため、下記の条件で実験を行った。

原水：ＴＯＣとしてイソプロピルアルコール４ｍｇＣ／リットルを含有する水

生物膜処理装置：固定床式好気性生物膜処理装置

膜分離装置：孔径０．２μｍのポリプロピレン製精密ろ過膜を用いた膜分離装置

【００３２】上記原水を生物膜処理装置によって生物処理し、過酸化水素水を生物処理水に添加した後、膜分離装置による処理を行った系［Ａ］と、過酸化水素水を添加しない以外は同様の処理を行った系［Ｂ］について、それぞれ定流量運転（１００リットル／m^2／ｈｒ）を行い、膜分離装置の膜間差圧を測定した。

【００３３】ただし、系［Ａ］においては、５０日目まで過酸化水素濃度が１０ｍｇ／リットルとなるように生物処理水に連続的に過酸化水素水を添加し、５１～７０日目では過酸化水素水の添加を停止し、７１～１００日目では再び過酸化水素濃度が１０ｍｇ／リットルとなるように生物処理水に連続的に過酸化水素水を添加した。また、系［Ｂ］においては、膜間差圧が１００ＫＰａに

達した後、過酸化水素濃度が１０ｍｇ／リットルになるように生物処理水に連続的に過酸化水素水を添加した。結果を図２に示す。図２において、Ａは系［Ａ］の結果、Ｂは系［Ｂ］の結果である。

【００３４】系［Ａ］及び［Ｂ］の結果より、過酸化水素濃度が１０ｍｇ／リットルになるように生物処理水に過酸化水素水を添加することにより、過酸化水素水を添加しない場合に比べて分離膜の膜ろ過効率が大幅に改善されることがわかる。

【００３５】また、系［Ａ］の結果より、過酸化水素水の供給を途中で停止してもすぐには膜間差圧が上昇せず、生物処理水への過酸化水素水の添加は間欠的に行っても効果があることが明らかになった。

【００３６】さらに、系［Ｂ］の結果より、膜間差圧が上昇した時点で生物処理水に過酸化水素水を注入することにより、膜間差圧の低下が認められ、したがって膜分離装置の運転を続けながら膜の洗浄を行い、劣化した膜間差圧を回復することが可能であることが明らかになった。これまで膜の薬品洗浄は、通常１～３ヶ月に１度の頻度で実施していたが、上記方法により薬品洗浄の頻度を６～１２ヶ月に１度の頻度に低減することが可能となり、水回収率の上昇及び回収システムの安定運転に大きく貢献すると考えられる。

【００３７】［実験例２］生物処理水中の過酸化水素濃度と、分離膜のろ過比抵抗との関係を検討した。

生物処理水：混合培養系の菌を用いた活性汚泥処理水の上澄み水

菌数＝２×１０^{6}個／ｍｌ

膜分離装置：孔径０．２μｍの酢酸セルロース系精密ろ過膜（アドバンテック社製）を用いた膜分離装置

ろ過方法：定圧加圧ろ過

【００３８】上記の条件で、生物処理水への過酸化水素水添加量を変えながらろ過を行い、過酸化水素濃度とろ過比抵抗との関係を調べた。結果を図３に示す。図３より、過酸化水素濃度が１～１００ｍｇ／リットルの範囲で膜ろ過効率が改善され、１００ｍｇ／リットルを超えると逆に膜ろ過効率が悪くなることが明らかである。

【００３９】［実験例３］以下の条件で、生物処理水への過酸化水素水の添加及び次亜塩素酸塩の添加が超純水製造システムに及ぼす影響について検討した。

原水：ＴＯＣとしてイソプロピルアルコール４ｍｇＣ／リットルを含む水

超純水製造システム：原水→生物膜処理装置→限外ろ過膜装置①→活性炭吸着塔→逆浸透膜装置→イオン交換装置→限外ろ過膜装置②

生物膜処理装置：固定床式好気性生物膜処理装置

限外ろ過膜装置①②：ポリアクリロニトリル製限外ろ過膜を用いた膜分離装置

【００４０】上記の超純水製造システムにおいて、生物膜処理装置と限外ろ過膜装置①との間で生物処理水に過

酸化水素濃度が１ｍｇ／リットルとなるように過酸化水素水を連続的に添加したシステム［Ｘ］、及び、同じ箇所で生物処理水中に次亜塩素酸ナトリウムを残留塩素濃度が１ｍｇ／リットルとなるように連続的に添加したシステム［Ｙ］とにより、それぞれ超純水を製造した。

【００４１】その結果、末端超純水（限外ろ過膜装置②による処理後の処理水）のＴＯＣは、システム［Ｘ］では１μｇＣ／リットル、システム［Ｙ］では３μｇＣ／リットルであった。これらの末端超純水中の有機塩素化合物をそれぞれＧＣ－ＭＳで測定したところ、システム［Ｘ］の超純水からは、有機塩素化合物は検出されなかった。これに対し、システム［Ｙ］の超純水からは、ＴＯＣとして約２μｇＣ／リットルのトリクロロエチレンが検出された。

【００４２】上記の結果から、生物処理水への次亜塩素酸塩の添加により有機塩素化合物が生成し、これが末端超純水にリークしてその水質を低下させることが明らかになった。一方、生物処理水への過酸化水素水の添加は、末端超純水の水質を低下させないものであった。

【００４３】

【発明の効果】本発明の水処理方法によれば、好気性生物膜処理装置による生物処理水を膜分離装置で処理する場合において、膜分離装置の運転を停止することなく、通常の膜分離処理を行いながら、分離膜の膜ろ過効率を改善することができる。したがって、本発明によれば、膜分離装置の高フラックスの維持、薬品洗浄の頻度低減が可能となり、水処理効率の向上、水処理システムの安定運転を達成することができる。さらに、膜ろ過効率を向上させて高いフラックスを得ることにより、システムのコストダウン及びスペースダウンにもつながる。

【００４４】また、本発明方法は、塩素剤を用いる方法のように有機塩素化合物を生成させることがなく、超純水回収システムに適用した場合に得られる純水あるいは超純水の水質低下を生じさせることがない上、塩素に対して耐久性のない分離膜にも適用できる。したがって、本発明は、半導体工場や液晶工場のプロセス用水として使用される超純水の回収システムにおいてきわめて有効な水処理方法である。

【図面の簡単な説明】

【図１】図１は、本発明の実施に用いる水処理システムの一例を示すフロー図である。

【図２】図２は、生物処理水に過酸化水素水を添加した場合及び添加しない場合における分離膜の膜間差圧の変化を示すグラフである。

【図３】図３は、生物処理水の過酸化水素濃度とろ過比抵抗との関係を示すグラフである。

【符号の説明】

４　原水槽

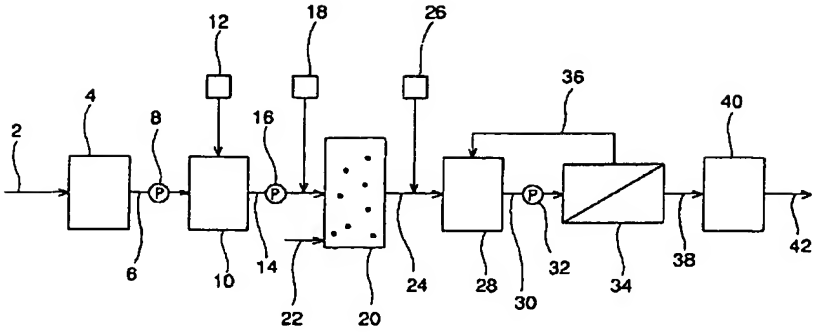
１０　ｐＨ調整槽

１２　酸・アルカリ注入ユニット

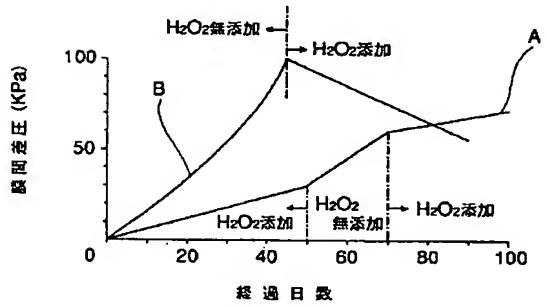
9　　10

１８　窒素・リン注入ユニット　　＊２８　生物処理水槽
２０　好気性生物膜処理装置　　３４　膜分離装置
２６　過酸化水素水注入ユニット　＊　４０　処理水槽

【図１】



【図２】



【図３】